



Epoxy Nano-Reinforced Composite Systems

by Nicole E. Zander

ARL-CR-601

February 2008

prepared by

**Dynamic Science, Inc.
8433 N. Black Canyon Highway
Phoenix, AZ 85021**

under contract

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14. ABSTRACT Mechanical properties of epoxy nanocomposite systems were evaluated for nanoclay platelets, nanosilica spheres, and carbon nanotube fillers. The effect of surface modifiers, such as quaternary ammonium salts and epoxy groups, was examined. The Young's modulus and tensile strength for epoxy-clay systems are dependent on the chain length of the alkylammonium modifier. Longer chains allowed better intercalation and mechanical properties. For nanosilica composites, interparticle distance played a key role in the toughness of the composite. Peak performance of the composite was achieved when the spacing between particles equaled the particle diameter. Surface modification with pendant epoxy groups allowed the particles to react into the matrix with the curing agent and achieve proper dispersion. Carbon nanotubes were dispersed in the epoxy matrix via a plasma treatment that afforded free radical sites for maleic anhydride grafting. Higher modulus, strength, and 2 orders of magnitude higher conductivity were observed for the functionalized carbon nanotubes.					
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1. Introduction

Thermosetting epoxies are low-density polymers with excellent adhesive properties. They are widely used in adhesives, coatings, and electrical and plumbing parts (1). The polymers' brittleness upon curing is one major drawback that prevents wider applications of epoxies (2). Adding reinforcements such as nanoplatelets, nanoparticles, and carbon nanotubes has attracted considerable attention as a means to enhance the properties and overcome the limitations of epoxy resins. Nano-reinforcements, as opposed to traditional reinforcements, have been shown to improve the mechanical and thermal properties at much lower filler-loading levels (1). Due to the exceptionally high surface area of the nanofillers, the interphase region between the matrix and the filler comprises a considerable portion of the composite. Thus particle-matrix adhesion is crucial for proper stress transfer from the matrix to the filler of the applied loads. In addition, sufficient particle dispersion is essential for effective improvement of the composite's properties (3, 4). This report will briefly outline composite preparation methods and focus on the effect of adding several different types of nanofillers into an epoxy matrix. The findings also cover how particle dispersion and particle-matrix affinity influence these properties.

2. Synthesis

The correct synthesis method is critical in order to achieve the desired composite properties. The majority of nanocomposites are made by direct mixing—the filler is mechanically mixed with the epoxy resin without solvents (5). The curing agent is added, and the mixture is degassed and cured at an elevated temperature. Although this is the simplest and most cost-effective method, particle agglomeration and incomplete intercalation (of platelets) occurs. Using a solvent in the mixing step helps break up aggregated particles but must be removed before adding the curing agent. In addition, ultra-high shear mixers often break many of the platelet-type fillers, reducing their aspect ratios and reinforcing efficacy (6). Researchers have reported that a combination of solvent, mixing, and sonicating proves to be a much better method for dispersing and exfoliating the fillers (5, 7). Other researchers have reported in situ polymerization techniques as the most efficient way to prepare thermoset composites (8). For nanoclays, once a low-viscosity curing agent has swollen the clay galleries, epoxy prepolymer is added. The monomers diffuse into the clay galleries, intercalating the platelets. Further diffusion can lead to exfoliation, causing the platelets to disperse evenly throughout the matrix. In addition to the preparation method, the nature of the curing agent (hydrophobicity, structure), the polarity of the epoxy monomer, the cure temperature, and the surface treatments of the filler all play a role in determining the level of dispersion and extent of adhesion, which, in turn, dictate the composite properties (8).

3. Epoxy-Layered Silicate Platelets

Extensive studies have been performed on layered silicate in epoxy resins due to the relatively low cost and ease of preparing such composites with greatly enhanced mechanical properties (8, 9). Montmorillonite clay (MMT), a naturally occurring and thoroughly examined layered silicate, will be the focus of this section of the report. These positively charged clays are typically treated with alkylammonium compounds to facilitate platelet separation and provide space for epoxy diffusion. The nature of the curing agent, the cure temperature, and the surface treatment of the filler all play a roll in the degree of intercalation and exfoliation. As will be discussed in subsequent paragraphs, exfoliated nanocomposites achieve enhanced mechanical properties over their intercalated counterparts.

Boukerrou et al. compared untreated MMT to an octadecylammonium-modified MMT. Figures 1 and 2 display transmission electron microscope (TEM) images of the respective nanocomposites (8). A much greater degree of agglomeration is seen in the untreated MMT composite (figure 1). The large surface energy difference between the unmodified clay and the polymer probably drives the particles to agglomerate. The absense of intercalating alkylammonium agents could also be a contributing factor. Although Young's modulus, as well as stress and elongation at break for the MMT composite, was improved compared to neat epoxy, the organomodified MMT showed a 20% improvement over the unmodified clay, owing to its greater degree of exfoliation and thus more surface area of the stiffening clay exposed to the matrix (8). Addition of the organoclay in all cases reduced the Tg of the composite due to the plasticizing effect of the alkyl chains or the disruption of the crosslinked epoxy structure.

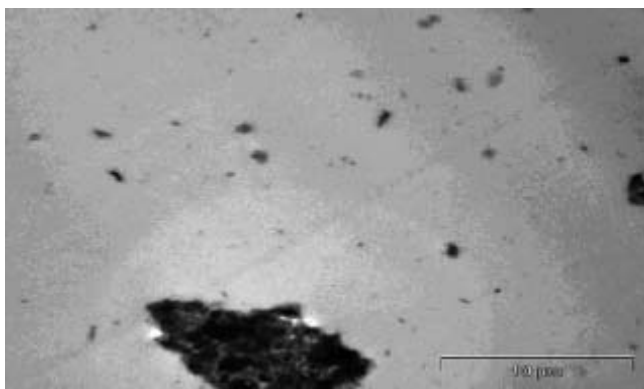


Figure 1. TEM image of the DGEBA/D2000/MMT nanocomposite.

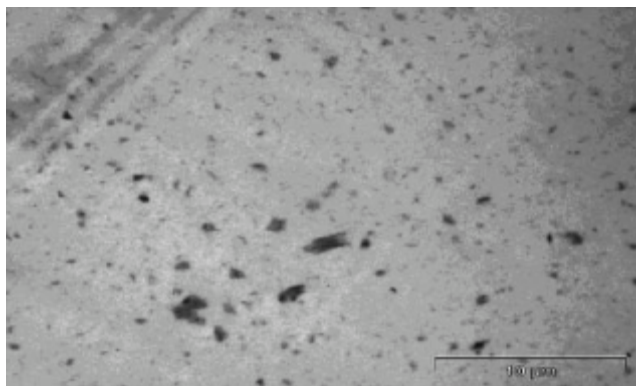


Figure 2. TEM image of the DGEBA/D2000/MMTC18 nanocomposite.

Researchers at Michigan State found that the degree of exfoliation depends on the chain length of the alkylammonium compound (10). Lan and Pinnavaia examined three different organoammonium chain lengths ranging from 7 to 17 carbons. Examining the x-ray diffraction patterns of the C7 and C17 clays, displayed in figures 3A and 3B, revealed several interesting factors (10). First, the basal spacing for the shorter chain-modified clay remains at a constant 15.2 Å throughout the cure process, whereas the longer alkyl-modified clay's spacing increases from 18 Å to 54 Å and finally disappears at the end of the cure cycle. Thus a near fully exfoliated nanocomposite is achieved with the C17 modification, but only an intercalated composite emerges from the C7 clay. The researchers found that for the longer chain organoclay, post-curing of the sample causes further polymerization which is catalyzed by the acidic primary amine. For the C7 clay, the hydrophobicity of the galleries is too low to promote adequate epoxy diffusion for exfoliation.

Tensile strength and modulus were examined for the C7, C11, and C17 organoclay composites at 10 weight-percent loading, and the results are displayed in figure 4 (10). The dashed lines indicate the respective strength and modulus in the neat epoxy. Although only three chain lengths were examined, there does appear to be a clear trend showing that chain lengths greater than 12 carbons are necessary to maximize the nanofiller's reinforcement ability. Based on this work, the tensile modulus for C12 and C17 falls within the error bars. This suggests no further improvement beyond 12 carbons. However, examining additional chain lengths would give a clearer picture of the tensile strength. It is difficult to decipher whether the tensile strength is leveling off at 17 carbons or whether an examination with an even longer alkyl chain might be warranted. Researchers at Texas A&M have confirmed this trend in epoxies with zirconium platelets, suggesting that the longer-chained amines create a more flexible interface and less brittle composite (11).

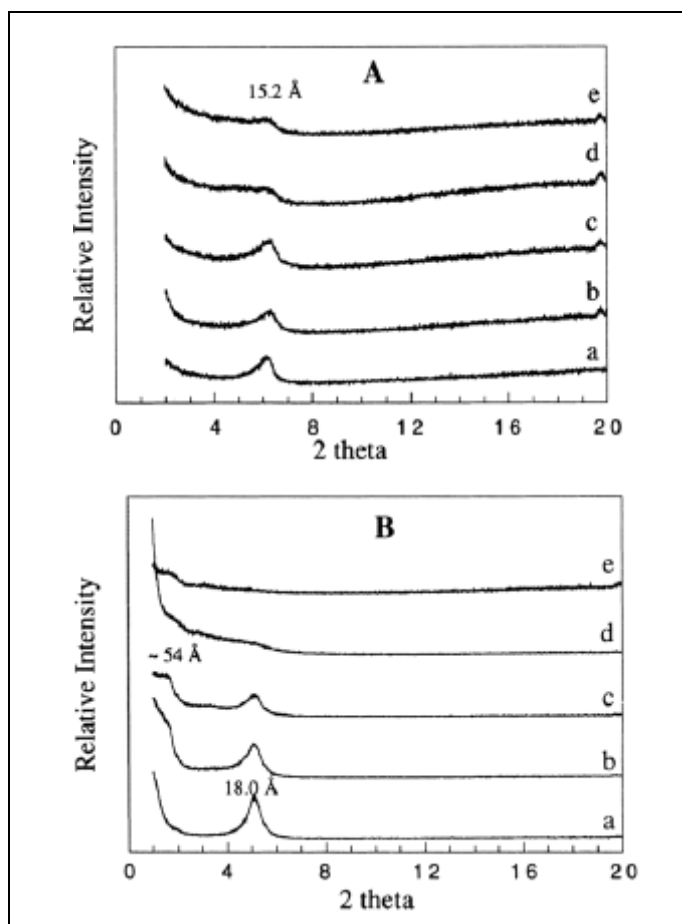


Figure 3. X-ray diffraction patterns of (A) $\text{CH}_3(\text{CH}_2)_7\text{NH}_3^+$ -MMT and (B) $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3^+$ -MMT in stoichiometric mixtures of epoxy resin and polyetheramine curing agent under the following conditions: (a) 75 °C, 10 min (b) 75 °C, 1 hr (c) 75 °C, 3 hr (d) 75 °C, 3 hr and 125 °C, 1 hr (e) 75 °C, 3 hr and 125 °C, 3 hr.

As alluded to in the Michigan State study, the cure temperature is another important factor to consider when preparing nanoclay composites. Ngo et al. examined two nanoclays, Nanomer^{*} I30E (MMT treated with octadecylamine, a primary amine base) and Cloisite[†] 30B (MMT treated with methyl tallow bis-[2-hydroxyethyl] quaternary ammonium) (12). The researchers examined two cure methods consisting of a room temperature cure and an elevated cure at 120 °C with post-cure at 140 °C. Table 1 displays the gallery distances for both clays at the different cure conditions (12). M1 and M2 denote room temperature and elevated temperature mixing during the composite preparation, respectively. The original gallery distances for each of the clays are displayed in the center column. The greatest platelet separations are achieved with

^{*}Nanomer is a registered trademark of Nanocor, Inc.

[†]Cloisite is a registered trademark of Southern Clay Products, Inc.

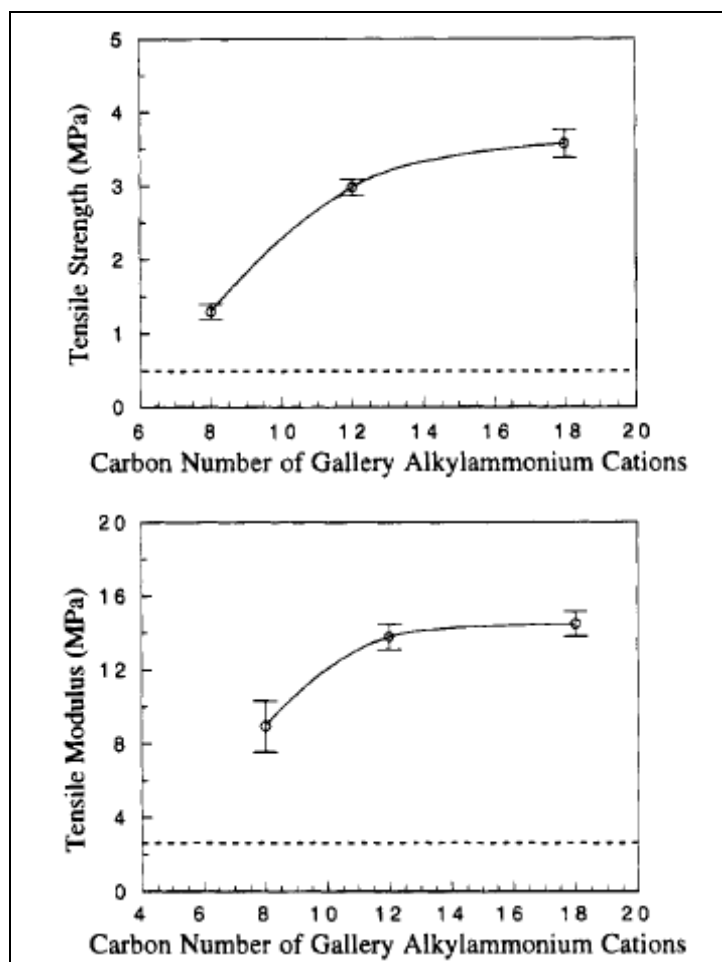


Figure 4. Dependence on chain length of alkylammonium ions:
(a) tensile strength and (b) modulus.

Table 1. Summary of x-ray diffraction data.

Sample	Gallery Distance (nm)		
	Cured at Room Temperature	Original Distance	Cured at 120 °C for 2 hr
SEP	—	—	—
Cloisite 30B	—	1.85	—
8EP-2pB-M1	3.99	—	4.38
8EP-2pB-M2	4.23	—	4.48
8EP-4pB-M2	4.17	—	4.41
Nanomer 1.30E	—	2.38	—
8EP-2pE-M1	4.84	—	5.60
8EP-2pE-M2	4.94	—	5.70
8EP-4pE-M2	4.70	—	4.99

the heated mixing and heated curing. The elevated temperature during mixing increases the molecular mobility and facilitates the diffusion of the epoxy and curing agent into the clay galleries. Thus greater intercalation and exfoliation of the composite is attained. Differential scanning calorimetry (DSC) data provides insight into why the I30E achieves greater gallery spacing over the 30B. The DSC curve shows that in the absence of a hardener, the I30E clay composite cured fully during the first heating cycle, unlike the other clay. The intercalating agent crosslinked with the epoxy and solidified the polymer. Hence, platelets became part of the epoxy-amine network, acting as bridges between crosslinks.

Data for the flexural modulus and strength of the two clay composites are shown in figure 5 (12). As previously described, M1 denotes room temperature mixing and M2 denotes elevated temperature mixing, with B indicating Cloisite 30B and E Nanomer I30E. The presence of the nanoclays increases the modulus of the composite compared to the pure epoxy. Compared to the 30B clay, the I30E clay gives a higher modulus at similar loading in both the high- and low-temperature mixing and cure, but the opposite holds true for the strength. For both I30E and 30B, the strength is higher for the elevated mixing, as the clay is better dispersed in the matrix, and there is less void space. The I30E exhibits a lower flexural strength, as it has a higher crosslink density and is a more brittle polymer. The polymerization of the epoxy with the primary amine attached to the clay most likely creates denser crosslinks around the particles. In addition, since the epoxy reacts with the organoclay, fewer reactions occur with the curing agent, leaving some free amines in the cured composite.

4. Epoxy-Nanosilica Spheres

Owing to their low cost and ease of surface modification for improved matrix adhesion, nanosilica particles comprise another important reinforcement for epoxy resins. Proper particle dispersion and separation are, in general, essential to obtaining the best mechanical properties of the composite. Several researchers have also found that interparticle distance contributes significantly to the composite toughness (13).

Particle dispersion is primarily controlled by surface modification to improve matrix compatibility and prevent agglomeration. Figure 6 displays a modified silica particle with epoxy end groups (14). These epoxy chain ends can form crosslinks when mixed with the curing agent, constructing a network around the particles. Figure 7 contrasts unmodified nanosilica to the epoxy-modified nanosilica (14). The surface-treated particles achieve greater and more uniform dispersion, whereas the unmodified particles tend to agglomerate.

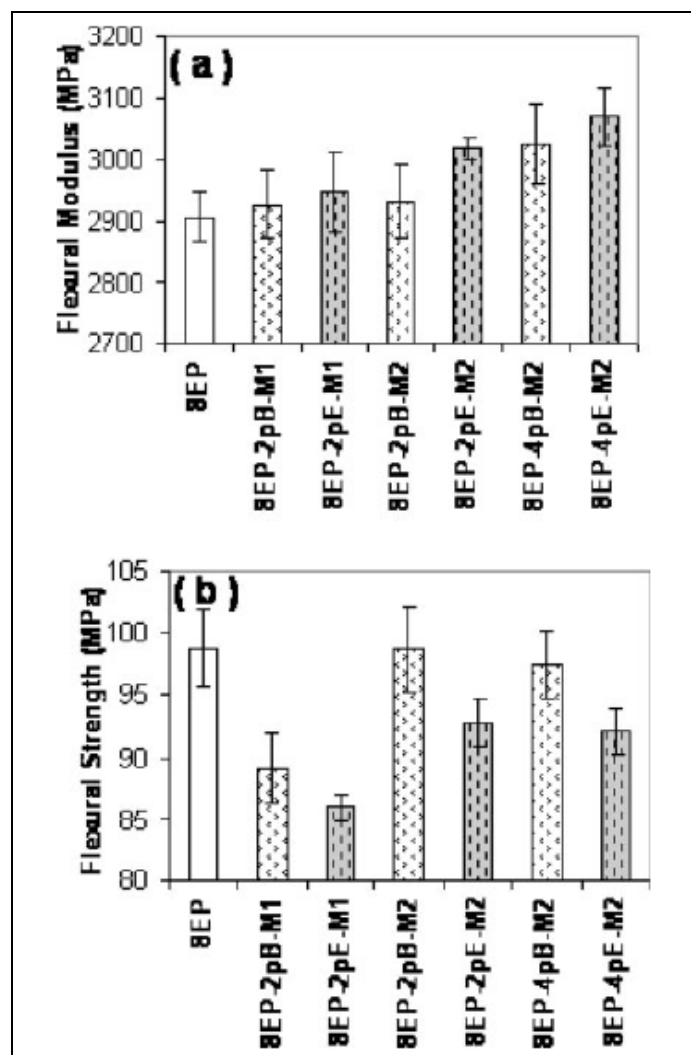


Figure 5. Flexural properties of EPON* 828 and its nanocomposites: (a) modulus and (b) strength.

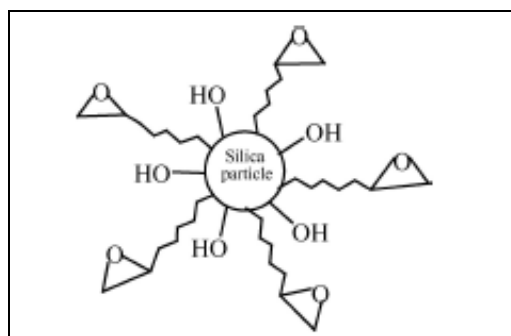


Figure 6. Chemical structure of the surface of the modified silica particles.

*EPON is a registered trademark of Shell Chemical Company.

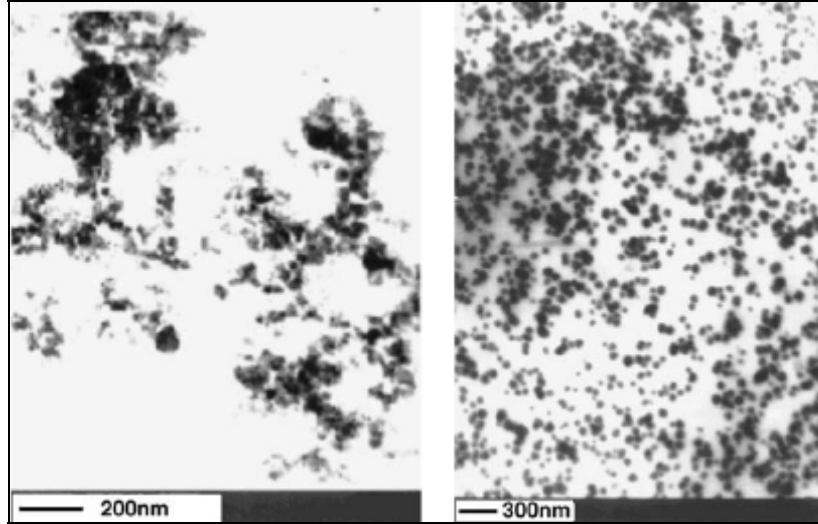


Figure 7. TEM images of nanosilica dispersed in an epoxy matrix: (left) unmodified and (right) modified.

Zhang et al. found that they could get good particle dispersion with up to 14 volume-percent loading without sacrificing optical clarity of the composite. Significant improvements were observed for flexural modulus, strength, microhardness, and toughness as can be seen in figure 8 (13). Impact resistance appears to peak about 3 volume-percent nanosilica. They also noted a slight decrease in the T_g with increasing silica content. The authors suggested that the particles could act as plasticizers, allowing for greater molecular mobility of the epoxy polymer chains in the interfacial regions. At high-filler loading, due to the high surface area to volume of these nanoparticles, the interfacial region comprises a significant portion of the composite and could be considered a third phase, in addition to the bulk matrix and nanofiller phases. The suppression of T_g in nanofilled composites has been observed by other researchers (13, 15).

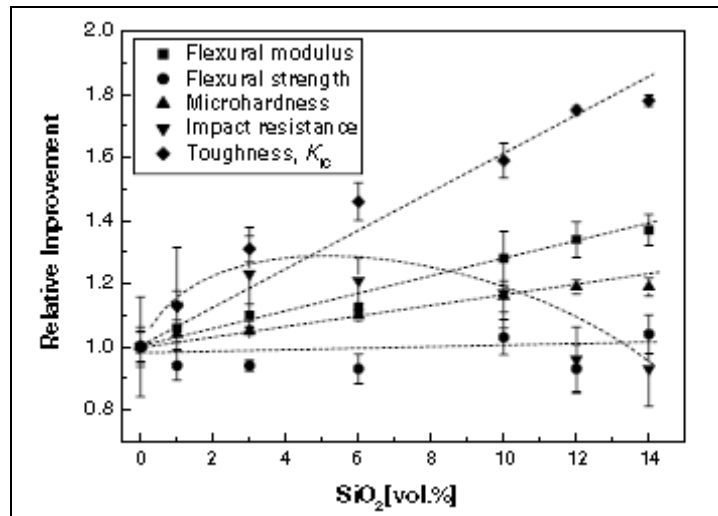


Figure 8. Relative improvements of various mechanical properties as a function of nanosilica volume fraction.

Zhang et al. also looked at the relationship between interparticle distance and several mechanical properties. A relationship between the interparticle distance, particle diameter, and loading can be drawn using the following equation:

$$\tau - d \left[\left(\frac{\pi}{6\phi_p} \right) \right]^{1/3} - 1, \quad (1)$$

in which d is the particle diameter, τ is the interparticle distance, and ϕ is the volume fraction of the particles. Results from the study of the impact of τ/d on flexural modulus and toughness are displayed in figure 9 (13). There appears to be a critical τ/d ratio equal to one, above which properties of the composite drop off significantly. Thus, when the spacing between the particles approaches the diameter of the particles, the reinforcement provides the greatest enhancement to the epoxy resin. The G_{IC} fracture toughness declines to the greatest extent, suggesting a further exploration of toughening mechanisms in these composites. The authors suggest a core-shell model, as shown in figure 10, in which the nanosilica is coated with strongly interacting polymer chains (13).

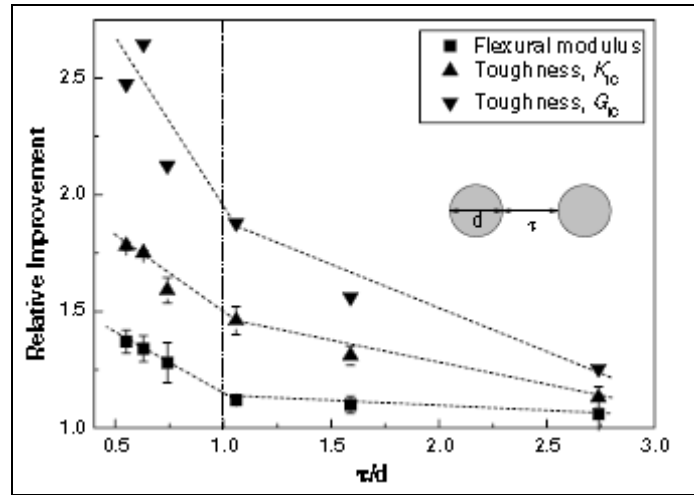


Figure 9. Correlations between interparticle distance and mechanical properties.

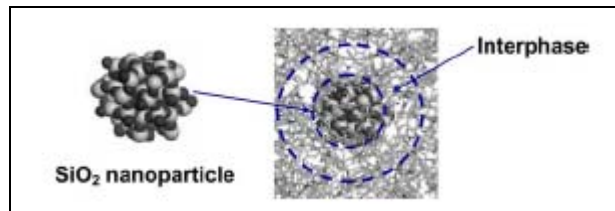


Figure 10. Structure of a core-shell building block of a silica nanoparticle coated with polymer chains.

When the τ/d reaches the critical ratio, the fracture mechanics are controlled by this core-shell structure, and this interphase region should be taken into account in modeling studies.

5. Epoxy-Carbon Nanotubes

Despite the high price of these materials, carbon nanotubes (CNTs) offer exceptional stiffening and strengthening abilities, with orders of magnitude higher than other traditional fillers or nanofillers. The major difficulty in optimizing composite properties with CNTs is achieving sufficient dispersion in the matrix (16). The strong van de Waals forces between the tubes tend to aggregate them in ropes and bundles, making them insoluble in most solvents and complicated to break apart with shear mixing.

Tseng et al. proposed a novel method to disperse the CNTs in an epoxy matrix using plasma (3). The plasma treatment afforded free radical sites available for grafting maleic anhydride (MA). The diamine curing agent ring opened the epoxide on the MA and was then able to undergo polymerization with the epoxy monomer, in effect becoming part of the epoxy matrix. This procedure is displayed in figure 11 (3).

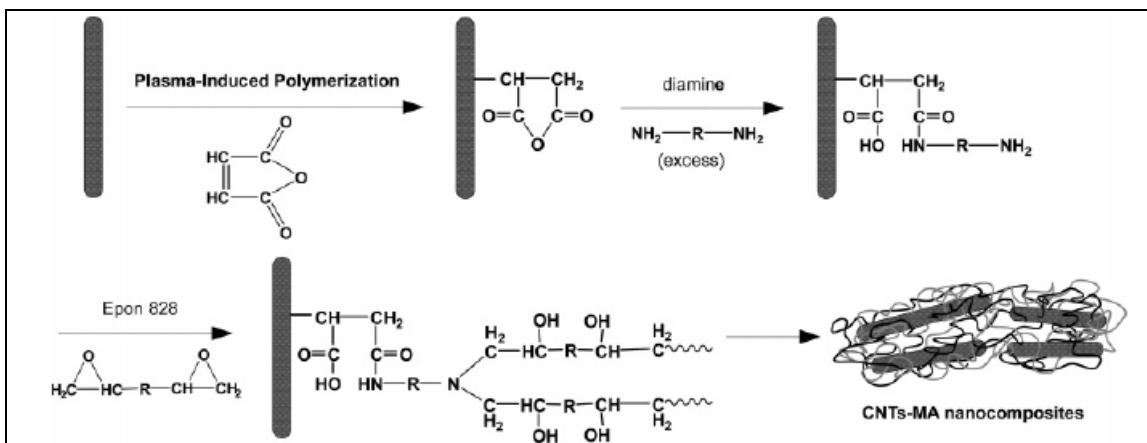


Figure 11. Procedure for the preparation of CNT-MA/epoxy nanocomposites.

A visual composite comparison of untreated vs. MA-treated CNTs reveals much about the dispersion of the CNTs within the epoxy. The untreated CNT composites are black and opaque even at 0.1 weight-percent loading, indicating a strong degree of aggregation of the CNTs. The MA-treated CNTs are transparent at the same loading, signaling better dispersion within the matrix. Compatibility for the MA-CNTs with the matrix was also demonstrated in fracture studies, as compared to the untreated CNTs, which displayed much more debonding from the matrix due to their poor adhesion. In addition, at 1 weight-percent loading, the MA-CNT

composites achieved 60% higher tensile strength, 40% higher elongation at break, higher tensile modulus, and greater thermal stability. Finally, the conductivity achieved for the MA-CNT composites was 2 orders of magnitude higher than the untreated CNTs. Better dispersion allowed the MA-CNTs to contact each other throughout the matrix and form a conductive network (3).

6. Conclusion

The ultimate goal of the nanofiller addition, or traditional filler for that matter, is to enhance the properties of the matrix. The degree to which this is done strongly depends on the dispersion of the additive throughout the matrix and the particle-matrix adhesion. The major advantage of nanosized fillers over traditional fillers is their nanodimensions. The large aspect ratios and high surface area to volume of nanofillers allow greater interaction with the matrix and similar or improved property enhancements at lower loading levels. Highly agglomerated particles lose their nanosized dimensions and start to behave as traditional fillers. The choice of synthesis method, such as direct mixing, solvent mixing, sonication, in situ polymerization, and surface modification of the filler, dictates the degree of dispersion and particle-matrix affinity. In addition, intercalating agents and cure temperatures greatly influence the properties of nanoclay-epoxy composites. As discussed previously, in almost all cases exfoliation and uniform dispersion improve the stiffness, strength, moduli, fracture toughness, and thermal stability.

Nanocomposites are still in their infancy, as critical problems such as determining the best preparation and dispersion methods are still being worked out. The high cost of materials, particularly carbon nanotubes, is a significant drawback. As this technology advances, the nanofiller market should see large growth and cost reduction as these additives are successfully applied to improve a myriad of polymeric systems.

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